

Complexation of Fullerenes on a Pentacene-Modified Au(111) Surface

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A novel method is proposed to prepare an ordered array of pentacene adlayer on a Au(111) electrode by self-organization in benzene solution without using an ultra-high-vacuum (UHV) system. Because of the electron-rich characteristic, the pentacene monolayer acts as a template to incorporate electron-accepting fullerenes, forming a stable C₆₀/pentacene complex adlayer. The adlayer structure was investigated by an in situ scanning tunneling microscopy (STM). Two adsorbed structures, ($\sqrt{31} \times \sqrt{13}$) and ($6 \times \sqrt{31}$), were observed for the pentacene adlayer. For the C₆₀/pentacene complex adlayer, molecular resolution STM revealed two ordered arrays, ($2\sqrt{3} \times 2\sqrt{3}$)R30° and “in phase” structures, for the C₆₀ molecules respected to the Au(111) substrate. The complex adlayer is stable between operational potential 0.35 and 0.9 V and is able to be decomplexed by selectively removing the fullerenes through the action of a high tip potential (0.75 V). The STM investigation also confirms that the complexation is performed by forming a C₆₀/pentacene/Au(111) nanoarchitecture. Scanning tunneling spectroscopy (STS) analysis reveals a semiconductive characteristic on pentacene and a rectifying behavior on the C₆₀/pentacene complex.

Introduction

The control and manipulation of material structure on the subnanometer scale is an essential requirement for designing molecular nanodevices. One of the crucial steps in the development of molecular-scale devices is the assembly and control of molecular components on solid substrates. The structure control of organic components on solid surfaces is always performed through the design and synthesis of molecules that form self-assembled monolayers on solid substrates. The adsorption of organic molecules into a two-dimensional (2D) ordered structure has been successfully investigated in a wide variety of systems.^{1–5} Nevertheless, the fabrication of a hierarchical structure of hybrid multi-layers comprising molecular-scale functionalities has rarely been investigated.^{6–8}

Fullerene-C₆₀ and pentacene have novel electronic properties that make them good candidates for the fabrication of

nanoscale electronic devices.^{8–13} If fullerene-C₆₀ can complex with pentacene to form an ordered array, it would be possible to obtain interesting physical and chemical properties to be employed in the fabrication of molecular devices. Supramolecular assembly of C₆₀^{13,14} and its derivatives¹⁴ on metal surfaces or semiconductor substrates has been intensively studied. However, only a few papers regarding the mixed 2D monolayers combining C₆₀ and other organic components have been reported recently.^{8,15–22} Organic materials with a macrocyclic structure, such as porphyrins,¹⁵ phthalocyanines,¹⁸ trimesic acid,¹⁹ calixarenes,^{20,8} cyclothiophene,²¹ and coronene,^{7b} were commonly used as template monolayers to form a complex with fullerenes. Because of the steric

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match with the molecular bearing of the host structure, fullerenes prefer to adsorb within the cavities of the macrocyclic molecules.^{19,20} A preferred complexation site on top of the conjugated rim of a macrocycle, governed by the formation of donor–acceptor complexes, was reported for cyclothiophene.²¹

To decipher the true host–guest interaction between the fullerenes and the host adsorbent, we used an ordered adlayer of pentacene as a template monolayer instead of a macrocyclic adsorbent. Pentacene is an electron-donating molecule. Therefore, C₆₀ molecules are expected to adsorb on a pentacene-modified surface through the donor–acceptor interaction, leading to a supramolecularly assembled system.

Ordered structures of pentacene films have typically been prepared in an ultra-high-vacuum (UHV) environment.^{10a,23,24} The results obtained in the UHV system imply the possibility of preparing an adlayer of pentacene on the Au surface in a solution system. However, no report regarding the self-assembled technique in a solution has been found for the pentacene adlayer.

In the present work, a new approach to preparing ordered adlayers of pentacene by self-organization in a proper solvent without using the UHV system is proposed. Furthermore, fullerene-C₆₀ was self-assembled on a well-defined pentacene template. The adsorbed structures of pentacene/Au(111) and C₆₀/pentacene/Au(111) adlayers, as well as their electronic properties, were investigated by scanning tunneling microscopy (STM). To the best of our knowledge, this is the first study preparing an ordered pentacene adlayer without using the UHV system and the first that successfully organizes C₆₀ on a pentacene-modified substrate.

Experimental Section

The cyclic voltammetry was performed with a CHI-703 potentiostat (Austin, TX). The STM used was a Nanoscope-E (Digital instruments, Santa Barbara, CA) with a single tube scanner (high-resolution A-head, maximum scan area 500–600 nm). The tip was made of tungsten (diameter 0.25 mm), which was prepared by electrochemical etching in 2 M KOH, and a thin layer of nail polish was applied to minimize residual faradic current. Constant-current mode was always used in the STM imaging experiments. This operation mode was able to capture high-quality STM images.

The gold single-crystal bead was obtained by melting the end of an Au wire according to a procedure described previously.²⁵ The pentacene adlayer was formed by immersing an Au(111) electrode into a 1 mM pentacene–benzene solution for about 30 s. An adlayer of C₆₀ on the pentacene array was formed by successively immersing the pentacene/Au(111) electrode into a 1 mM C₆₀ benzene solution for 60 s. The adsorbed Au(111) electrode was then rinsed with ultrapure water, and finally transferred into an electrochemical STM cell or cyclic voltammetric (CV) cell filled with 0.1 M HClO₄.

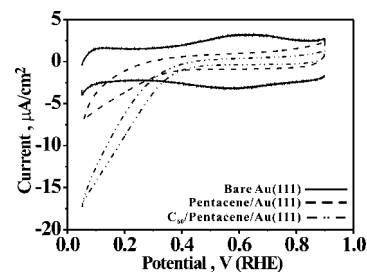


Figure 1. Typical cyclic voltammograms of bare Au(111) (solid line), pentacene-adsorbed Au(111) (dashed line), and C₆₀ adsorbed on pentacene-modified Au(111) (dotted dashed line) in pure 0.1 M HClO₄. The potential scan rate was 50 mV/s.

The STS experiments were performed in a liquid–solid interface. After imaging the adlayer, the scan process was stopped and the tip was moved to a position on top of the ordered molecule. The sample was grounded and the feedback loop was closed. The tip–sample distance was initially adjusted by setting a tip voltage (–0.6 V) and a low tunneling current (150 pA). After a waiting period for stabilizing the system, a voltage scan from –1.5 to 1.5 V was applied on the tip and the tunneling current was recorded. For an adlayer, the STS experiments were performed at various positions, and the consistent results obtained from independent experiments confirm the reproducibility of the data.

Results and Discussion

Figure 1 shows the cyclic voltammograms (CVs) of a well-defined Au(111) electrode (solid line), an Au(111) electrode modified by pentacene (dashed line), and C₆₀/pentacene (dotted line) in 0.1 M HClO₄. They were recorded in a N₂ atmosphere at a scan rate of 50 mV/s. For the bare Au(111) electrode, the voltammogram in the double-layer potential region is identical to that reported for a single-crystal Au(111) surface.²⁶ The CV obtained for a pentacene-modified Au(111) shows a decrease in the double-layer charging current, indicating that the Au(111) surface is covered with a pentacene adlayer. The pentacene adlayer is stable in the featureless double-layer charging region between 0.3 and 0.9 V. The small reduction current commencing at 0.3 V might be due to partially reductive desorption of pentacene. However, it is inferred that the desorbed pentacene will readsorb during the anodic scan because the CV profile does not vary with the repetitive potential cycles between 0.05 and 0.9 V.

After a subsequent immersion of the pentacene/Au(111) electrode into a C₆₀ benzene solution for 1 min, the double-layer charging current decreases further to about half of the pentacene/Au(111) electrode. Because the charging current is proportional to the capacitance of the double layer, the capacitance of the C₆₀/pentacene complex layer decreases because of the incorporation of C₆₀. The C₆₀/pentacene complex layer is also stable between 0.35 and 0.9 V, and an apparently reductive peak commences at about 0.3 V. When the scanning was repeated between 0.05 and 0.9 V, the CV profile of the C₆₀/pentacene/Au(111) electrode became increasing similar to that of pentacene/Au(111), indicating that C₆₀ was continuously reduced and desorbed from the

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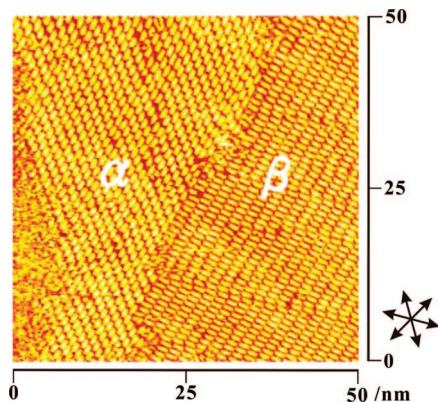


Figure 2. Large-scale STM images of the pentacene adlayer assembled on Au(111) by self-organization in a benzene solution.

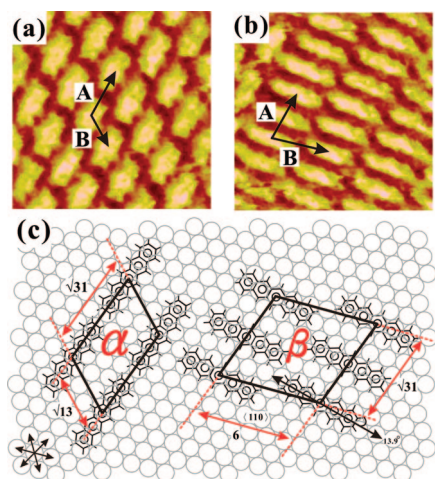


Figure 3. Higher-resolution STM images of pentacene adlayer with structures of (a) α and (b) β phases ($6 \times 6 \text{ nm}^2$). (c) Corresponding molecular structures of pentacene on the Au(111) surface for the two phases.

pentacene/Au(111) surface. This result also shows that the C_{60} /pentacene interaction is weaker than the interaction between pentacene and the Au(111) surface.

Figure 2 shows a typical large-scale STM image of the pentacene adlayer prepared by directly immersing the Au(111) electrode in a pentacene–benzene solution for 30 s. The image was acquired at 0.7 V in 0.1 M HClO_4 and the tip potential was kept at about 0.3 V. The atomically flat terraces were almost completely covered by an ordered adlayer of pentacene. Two different domains of distinct structures, termed α and β phases, were observed in Figure 2. The two structures were found in each independent experiment as demonstrated in Figures S1 and S2 in the Supporting Information. In Figure S1, the stacking rows of the two domains cross each other by ca. 14° , indicating that the two phases are not the rotation domains of the same structure. The high-resolution images acquired from the two ordered domains are shown in images a and b in Figure 3. The elongated feature of the molecular images reflects the molecular characteristic of a pentacene molecule. For the α and β phases, the longer molecular axis (C_2) of the pentacene align, respectively, along the $\sqrt{31}$ and $\sqrt{13}$ directions of the Au(111) surface. Each pentacene molecule interacts with its nearest neighbor in an end-to-end fashion.

For the α phase shown in Figure 3a, the molecular rows of the adlayer, **A** and **B**, align along the $\sqrt{31}$ and $\sqrt{13}$ direction, respectively. The center-to-center distances between the pentacene molecules in the two rows were measured to be 1.61 ± 0.01 and 1.04 ± 0.01 nm, corresponding to $\sqrt{31}$ and $\sqrt{13}$ times the interatomic spacing of the Au(111) substrate, respectively. The adlayer structure of the α phase was identified as $(\sqrt{31} \times \sqrt{13})$, and the model proposed is shown in Figure 3c. The surface coverage, defined as the ratio of adsorbed pentacene molecules to the Au atoms, is about 0.0476.

The high-resolution image of the β phase is shown in Figure 3b. One of the molecular rows (**A** direction) aligns in the $\sqrt{31}$ direction with an intermolecular spacing of 0.80 ± 0.02 nm. The second molecular row (**B** direction) aligns along the close-packed direction of the Au(111) substrate and the intermolecular distance was measured to be 1.75 ± 0.05 nm, equivalent to 6 times as large as the interatomic spacing of the Au substrate. The detailed molecular arrangement of the β phase on Au(111) is shown in Figure 3c and the adlayer structure was determined to be $(6 \times \sqrt{31})$. The surface coverage measured for the β phase is about 0.057. It is noteworthy that the molecular dimension of pentacene observed for α and β phases has a slight difference in Figure 3b. This difference is mainly attributed to the thermodrift that commonly presents in the STM imaging process. This effect of thermodrift on the molecular dimension for domains that have identical phase (α phase) but different orientations is demonstrated in Figure S2 in the Supporting Information.²⁷

The flat-lying orientation of pentacene on the Au electrode suggests that the driving force for the self-organization of pentacene on Au(111) is the interaction of the conjugated electrons of pentacene to the Au(111) substrate. It was reported that benzene molecules adsorb strongly on Pt and Rh electrodes²⁸ but do not adsorb on the Au(111) surface.²⁹ These results indicate that the π -electron/substrate interaction is dominated not only by the substrate but also by the number of aromatic ring contained in a molecule. Apparently, the multiaromatic rings of pentacene produce a stronger π -electron/Au(111) interaction compared with that of benzene/Au(111), which is responsible for the self-organization process. Compared with the variety of structures of the pentacene films prepared by vacuum deposition,^{5a,18} the pentacene adlayer prepared by the present method exhibits a more uniform and simple structure. The different adlayer structures obtained for the two systems are attributable to the different environments and mechanisms involved in formation of the admolecules. Apparently, the present method provides a convenient and feasible technique to produce a well-ordered molecular adlayer of pentacene, which may be important in the development of molecular electronics.

A fullerene- C_{60} adlayer was then self-organized on the pentacene-modified Au(111) electrode, and a typical image

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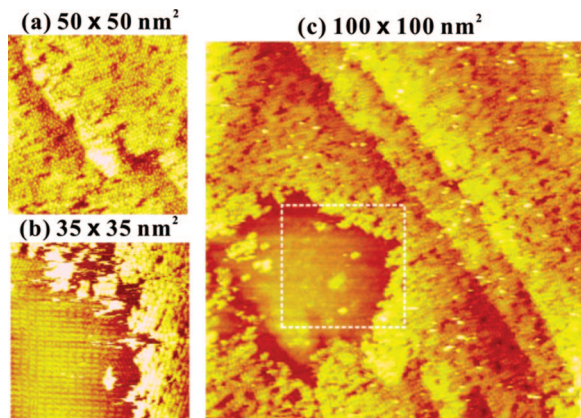


Figure 4. (a) In situ STM images of the C_{60} adlayer adsorbed on a pentacene/Au(111) electrode acquired in 0.1 M $HClO_4$ at 0.7 V. The tip potential is 0.3 V. (b) The image obtained after raising the tip potential to 0.75 V. The C_{60} adlayer was removed after several scans through the action of the tip and the structure of pentacene adlayer reappears. (c) The tip potential was turned back to 0.3 V and the image was zoomed out. The region without the action of the tip potential preserved the adsorbed image of C_{60} , which is different from the marked region that was subjected to the action of the tip.

obtained is shown in Figure 4a. The ordered array of pentacene disappeared, with another adlattice forming instead. The newly formed adlattice extends over an image of $100 \times 100 \text{ nm}^2$ and is believed to be the structure of C_{60} /pentacene complexes. To decipher the structure of the complex adlayer, decomplexation was attempted by raising the tip potential.³⁰ After several scans at a tip potential of 0.75 V, the adlattice of pentacene reappears as shown in the left region of Figure 4b, indicating the accomplishment of decomplexation by removing C_{60} without ruining the ordered adlattice of the pentacene template. On the basis of this result, this complexation is inferred to be performed by the adsorption of the C_{60} layer on top of the pentacene monolayer, forming a C_{60} /pentacene/Au(111) nanoarchitecture. The tip potential was then turned back to 0.3 V and the imaging was zoomed out to compare regions with and without the action of a high tip potential. The image in Figure 4c shows that the region without the scraping of a tip potential still preserved the structure of the C_{60} /pentacene complex, which is different from the regions that were subjected to the action of the STM tip (the region marked in Figure 4c).

The present result indicates that C_{60} successfully complexed with the pentacene adlayer. Pentacene is known to be a p-type organic semiconductor. The pentacene-modified Au(111) surface thus offers complexation sites for an n-type material, such as fullerene- C_{60} . This result also implies that the host-guest interaction between the pentacene and C_{60} is dominated by the donor-acceptor mechanism. The fact that the decomplexation of the complex is able to be performed by the action of a high tip potential offers the possibility of selectively etching the nanoarchitecture and patterning a surface comprising pentacene and C_{60} /pentacene adlayers.

Figure 5 shows the high-resolution image of C_{60} adsorbed on the pentacene/Au(111) surface. The patchy appearance of the C_{60} structure shown in Figure 5a indicates that the ordered domains are short range. This result may be caused

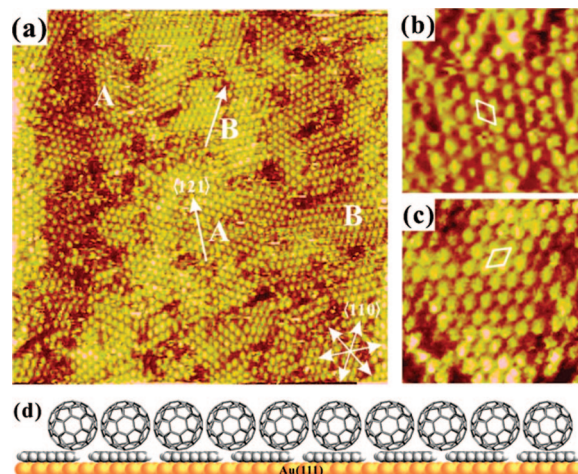


Figure 5. (a) Large-scale ($50 \times 50 \text{ nm}^2$) STM image of a C_{60} /pentacene adlayer on an Au(111) surface acquired in 0.1 M $HClO_4$ at 0.7 V. (b, c) Higher-resolution STM images ($10 \times 10 \text{ nm}^2$) acquired for domains (b) A and (c) B. (d) Structural model illustrating the nanoarchitecture of C_{60} /pentacene complexes assembled on Au(111).

by the presence of various structures in the template pentacene layer, and/or by the mismatch of lattice parameters between C_{60} and pentacene adlayers that will be discussed below. In Figure 5a, two different structures, A and B, can be observed. The molecular rows of the two structures cross each other at an angle of 30° within an experimental error of $\pm 3^\circ$. The higher-resolution scan was acquired for domain A and shown in Figure 5b. The molecular rows of this structure were found to run parallel to $\langle 110 \rangle$, the $\sqrt{3}$ direction of Au(111). The intermolecular spacing was measured to be 1.01–1.04 nm, corresponding to $2\sqrt{3}$ times the lattice constant of Au(111). Therefore, a structure of $(2\sqrt{3} \times 2\sqrt{3})R30^\circ$ was assigned to this phase. The high-resolution images acquired for domain B are shown in Figure 5c. The molecular rows of C_{60} in domain B are parallel to the $\langle 112 \rangle$ direction of the Au(111) surface. The intermolecular distances were measured to be 1.00–1.05 nm. A structure corresponding to this row direction and molecular distance was reported in the literature and is called the “in phase” structure.³¹ It is interesting to find that the structures of C_{60} assembled on a pentacene-modified Au(111) are identical to the structures of C_{60} directly adsorbed on the Au(111) surface,³¹ but different from the structures assembled on template monolayers prepared by macrocyclic molecules.^{5,7,8,19–21} This result seems to suggest that pentacene molecules have little constraint, than the other template monolayers using macrocyclic molecules, to the localization of C_{60} . Therefore, C_{60} molecules are able to organize into a structure similar to that on a bare Au(111) surface. At the present stage, it is difficult to obtain the exact location of C_{60} relative to pentacene. Because of the difference in the lattice parameters and structures obtained for C_{60} and pentacene adlayers, it is quite possible that C_{60} molecules do not have consistent locations relative to the pentacene. Considering simulta-

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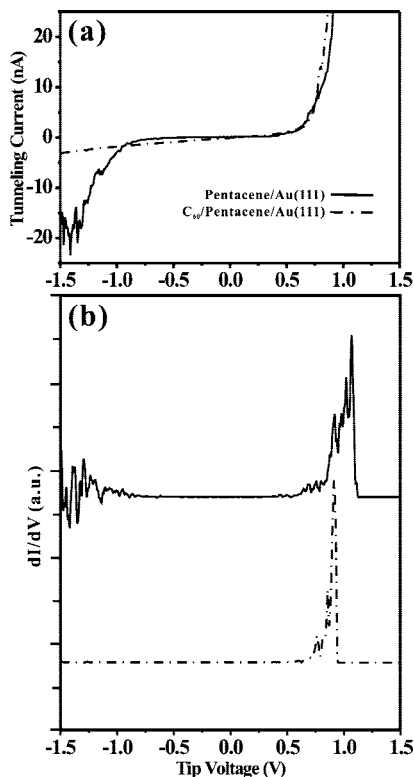


Figure 6. STS measurements on the pentacene and C_{60} /pentacene complex showing (a) the tunneling current (I) versus bias voltage (V), and (b) differential conductance (dI/dV) versus bias voltage (V). In the positive potential region higher than ca. 1 V, the tunneling current cannot be traced because of the limitation of equipment. Therefore, the dI/dV curves in this region represent a baseline.

neously the previous result that C_{60} molecules are adsorbed on the pentacene adlayer, we propose a simple model illustrating the inconsistent locations of C_{60} molecules on pentacene adlayer in Figure 5d.

The electronic properties of the pentacene and C_{60} /pentacene adlayers were explored by scanning tunneling spectroscopy (STS) at the liquid–solid interface.^{21,32} The bias voltage was applied to the tip, and the sweep began in the positive direction at -1.5 V. Repeated experiments were performed for an adlayer, and the reproducibility was confirmed by consistent results obtained from independent experiments. Figure 6 shows the current versus bias voltage (I – V) and the corresponding dI/dV result acquired between -1.5 and 1.5 V. It is noteworthy that because of the limitation of equipment, the tunneling current cannot be traced for potentials higher than ca. 1 V. Therefore, the dI/dV curves in this region represent a baseline. For pentacene, the asymmetric I – V curve and the zero-conducting region around the Fermi level reveal the semiconductive behavior of this

compound. The orbitals of pentacene adlayer corresponding to the HOMO and LUMO levels, determined from the differential curve (Figure 6b), are located 0.85 V above and 1.20 V below the Fermi level, respectively, indicating the electron-rich character of the pentacene adlayer. The HOMO–LUMO gap measured using the STS (about 2.05 V) is higher than the band gap of pentacene in the bulk phase (1.9 V).³³ For the C_{60} /pentacene complex, the I – V curve at the positive tip bias is located close to that of pentacene. However, the tunneling current is likely blocked at the negative bias. No apparent peak corresponding to the LUMO state was found for the complex. These results indicate that the HOMO state of the C_{60} /pentacene complex is similar to that of pentacene, and the LUMO level shift inhibits the tunneling of electrons from the tip to the LUMO level of the complex at the bias applied in the present study. It is inferred that the LUMO level of C_{60} is significantly elevated after accepting the electrons donated by the pentacene. The large difference between tunneling currents at the positive and negative bias implies the rectifying behavior of the complex adlayer. This property offers a possibility of employing this system in nanoscale electronic molecular devices.

Conclusion

An ordered adlayer of pentacene on a Au(111) surface was successfully prepared using the self-organization technique in a benzene solution. Furthermore, the pentacene-modified Au(111) surface can be used as a template to prepare a nanoarchitecture by complexation with C_{60} in a benzene solution. The complexation is performed through the donor–acceptor interaction between p-type pentacene and n-type fullerene- C_{60} , forming a stable complex adlayer. Selective decomplexation of the complexes can be performed by removing the C_{60} under the action of a high tip potential. The STS analysis shows that the C_{60} /pentacene complex has a rectifying effect to the tunneling current, which is different from the electronic property of pentacene. Such findings offer a flexible and convenient technique for the applications of the two compounds in molecular electronics.

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Supporting Information Available: Figures S1 and S2 (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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